# Addressing Internal "Shuttle" Effect: Electrolyte Design and Cathode Morphology Evolution in Lithium-Sulfur Batteries

**Perla B. Balbuena**

**Texas A&M University**

**June 8th, 2017**

**Project ID #: ES283**

# Overview

## Timeline

- Start date: October 1, 2014
- End date: September 30, 2017
- Percent complete: 83%

## Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials evolution during cycling
  - Lifetime of the cell

## Budget

- Total funding: $990,000
  - DOE share: $990,000
  - Contractor share: Personnel
- Funding received
  - FY16: $325,189
  - FY 17:$379,466

## Partners

- Interactions/ collaborations
  - Partha Mukherjee (TAMU Co-PI)
  - Vilas Pol (Purdue Univ., Co-PI)
  - M. Vijayakumar (PNNL)
- Project lead: TAMU

# Relevance/Objectives

- **Objective:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide (PS) shuttle with advanced cathode structure design.
- **FY 2017 goals**: Understand role of electrolyte including PS on anode reactivity; $Li_2S$ deposition modes and electronic conductivity; effects of S loading, cathode morphology, and S to electrolyte ration on electrochemical performance; experimental tests of membranes for PS retention; cell fabrication and test.

- **Addressing targets and barriers**:
  - New insights regarding the role of the electrolyte on Li plating and cathode passivation by $Li_2S$. Further investigation and test of PS retention materials.
- **Impact:**
  - Alternative electrolyte chemistries and improved cathode architectures to deliver Li/S cells operating for 500 cycles at efficiency greater than 80%.

# Relevance/Milestones

- a) Electrochemical modeling of cell performance with electrolyte and cathode parametric properties (Q1/Y3-Dec. 16) **Completed**
- b) Development of stable electrolytes. (Q2/Y3- March 17). **In progress.**
- c) Produce 3-5 grams of C/S composite material. (Q3/Y3-June 17). **In progress.**
- d) Complete the scale-up of cathode composites, cell construction and testing. (Q4/Y3-Sept.17)

# Approach/Strategy

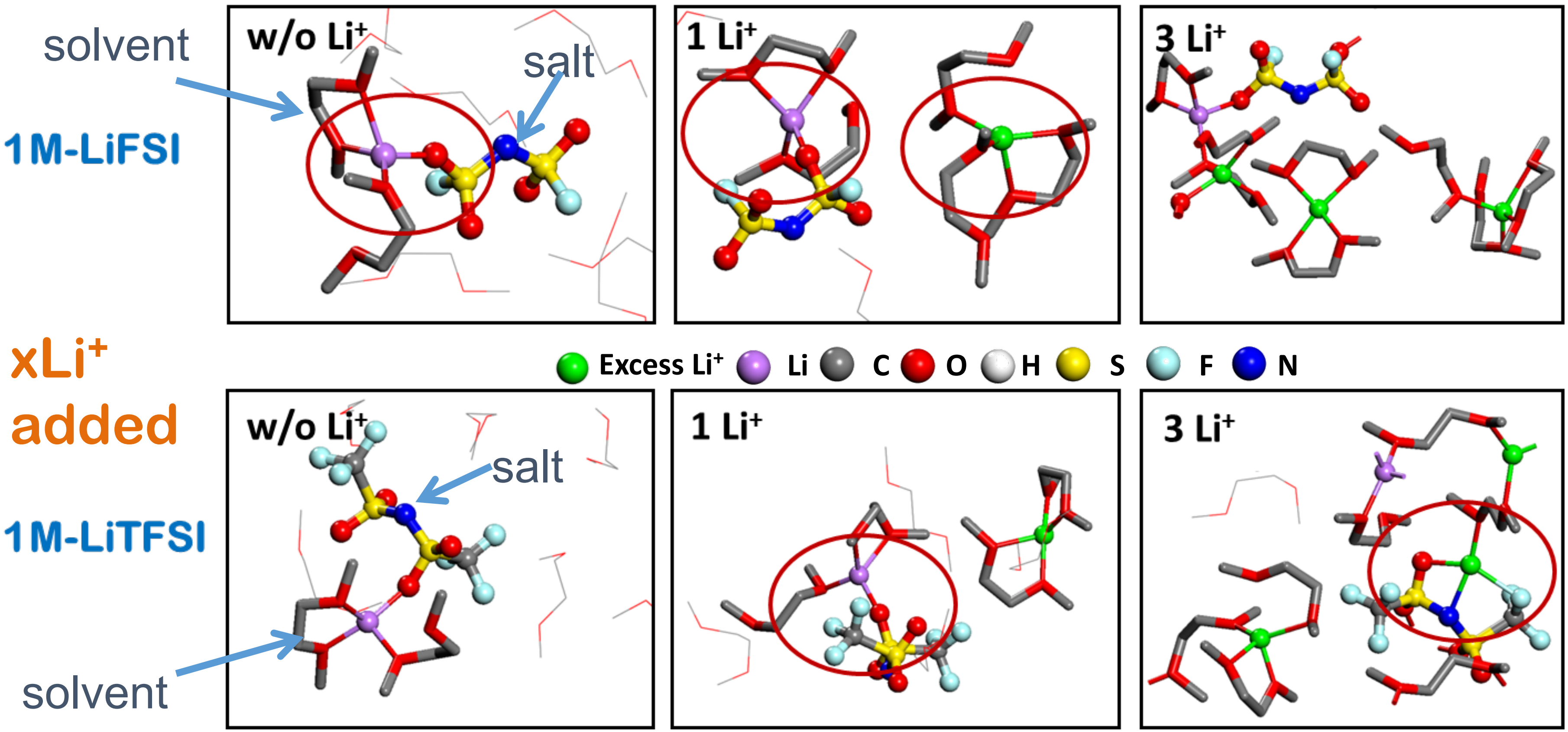
- **Overall Technical Approach/Strategy**:
  - A mesoscale model of electrode mesoporous structures based on stochastic reconstruction allows *virtual screening of cathode microstructural features* and effects on electronic/ionic conductivity and *morphological evolution*.
  - *Interfacial reactions at the anode* due to the presence of polysulfide species and effects on Li deposition characterized with ab initio methods.
  - Structural and energetic information from atomistic-level studies used in mesoscopic-level analysis of *cathode interfacial reactions*.
  - Novel materials for *PS retention* along with tuned porosity of cathode structures fabricated and tested on the basis of mesoscale and atomistic modeling efforts.

- **Progress towards FY17 milestones and Go/No Go decisions**: New understanding of interfacial anode chemistry and morphology effect on $Li_2S$ deposition reactions at the cathode. Analysis and test of materials for PS retention at the cathode.

# Technical Accomplishments: Barriers Addressed

- **Lifetime of the cell**
  - *Anion, solvent, and PS decomposition* at the Li metal anode in concentrated electrolyte solutions and effects on Li deposition during plating
- **Loss of available capacity**
  - Effects of S loading, S/electrolyte ratio, and cathode morphology on cell performance
  - Main electronic carriers in $Li_2S$ deposits
- **PS retention at cathode**
  - *Identified and tested specific materials* to retain soluble PS species at the cathode

# Technical Accomplishments
## Solvation effects in 1M solutions




**Salts do not totally dissociate (agrees with our DFT prediction)**
**Excess of Li$^+$ → compact and complex coordinated networks**
**First shell of Li$^+$ dominated by solvent**

**Milestone Q2/Y3:** Development of stable electrolytes ✓



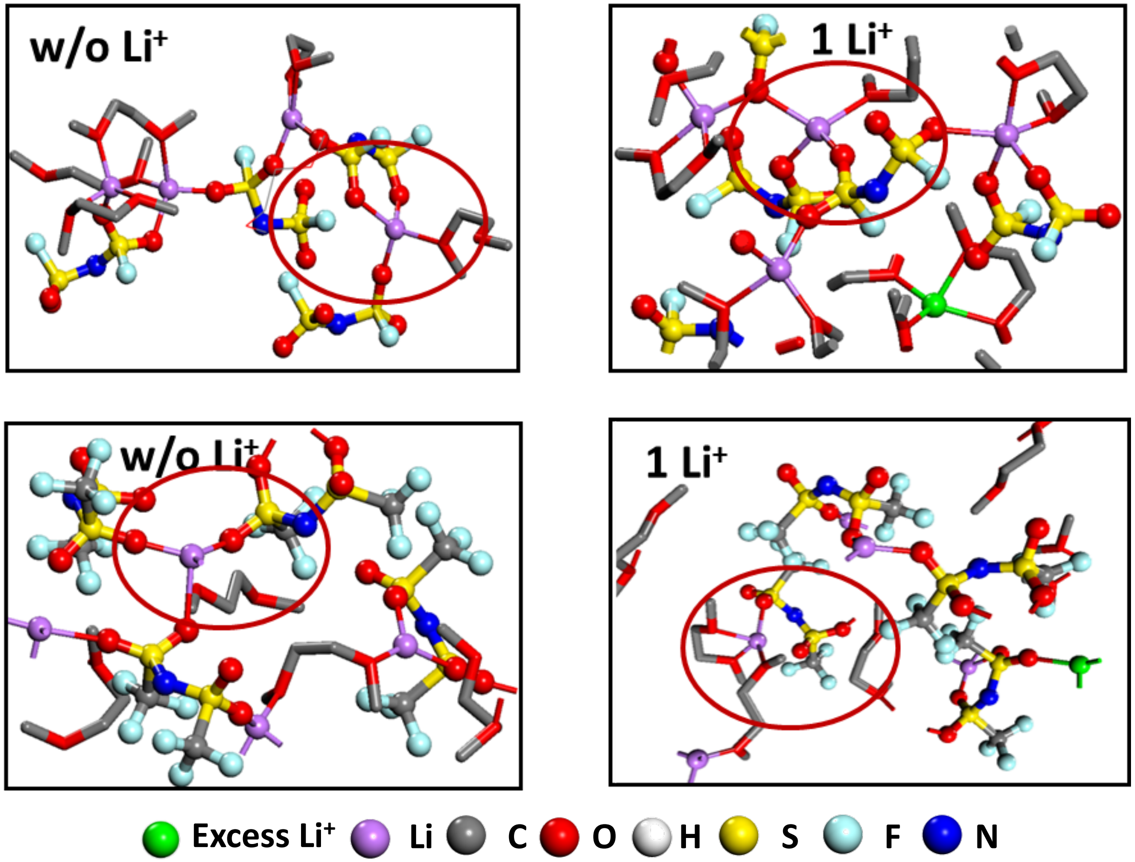
Camacho-Forero *et al*. JPCC, 121, 182-194, 2017

# Technical Accomplishments
## Solvation effects in 4M solutions

**4M-LiFSI**

**xLi+ added**

**4M-LiTFSI**




Much **more complex networks** than those for 1M

Almost all the species **interconnected**

Some salt molecules transition from *trans-* structures to *cis-*

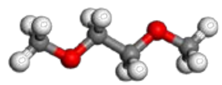
**Mixed coordination numbers** (solvent + salt)

**Milestone Q2/Y3:** Development of stable electrolytes

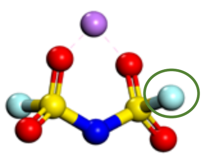


**Camacho-Forero** *et al*. JPCC, 121, 182-194, 2017

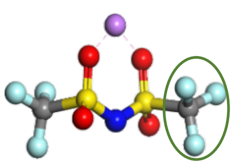
# Technical Accomplishments
# Solvation & reaction at the Li surface



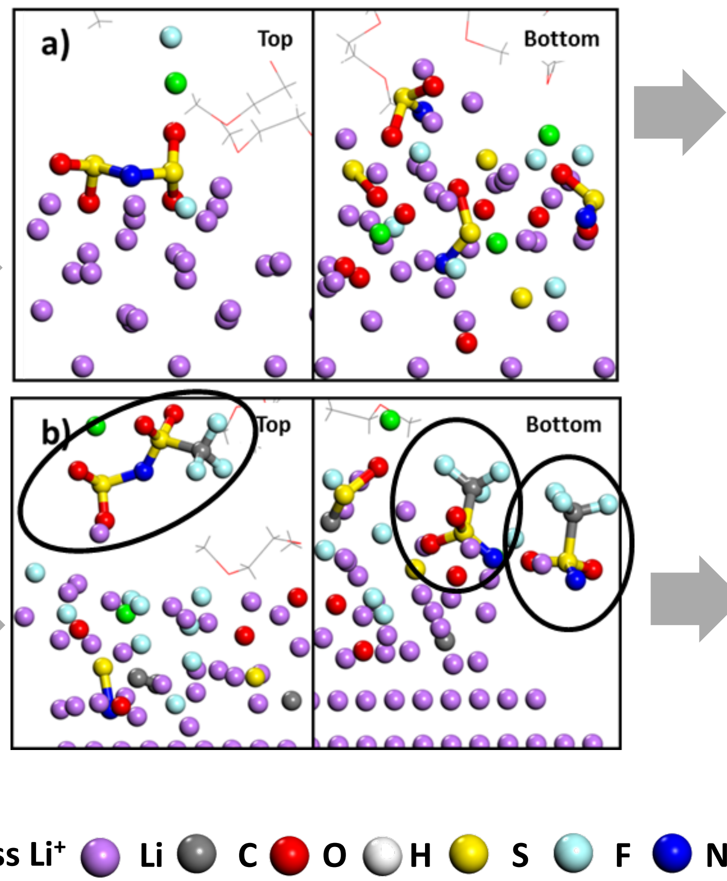
Solvent: DME



LiFSI



LiTFSI




- More compact SEI
- All F atoms in the SEI
- LiFSI → LiF-based SEI-layer more efficiently than LiTFSI

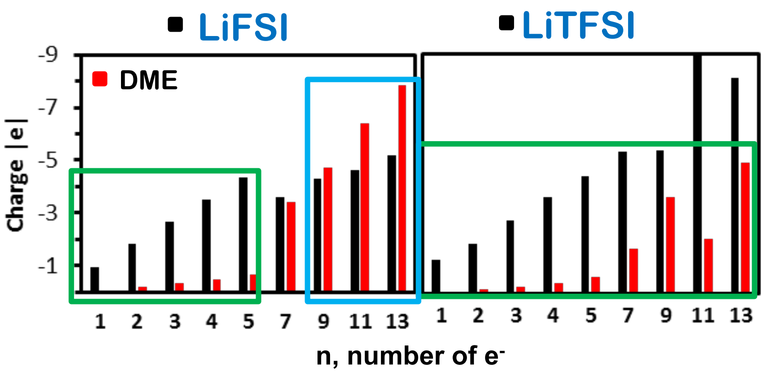
- Large fragments: $CF_3SO_2N$ and $CF_3SO_2NSO_2$
- C-based compounds in SEI
- Several $CF_3$ groups remain
- Higher charge transfer found from reactions involving reduction of C-atoms

**Milestone Q2/Y3:** Development of stable electrolytes

Camacho-Forero *et al*. JPCC, 121, 182-194, 2017

# Technical Accomplishments:

## Solvent vs. Salt Reduction – Effects of Concentrated Salt Solutions




**DME reduces much later than the anion; and the extent of the reduction depends on the salt**

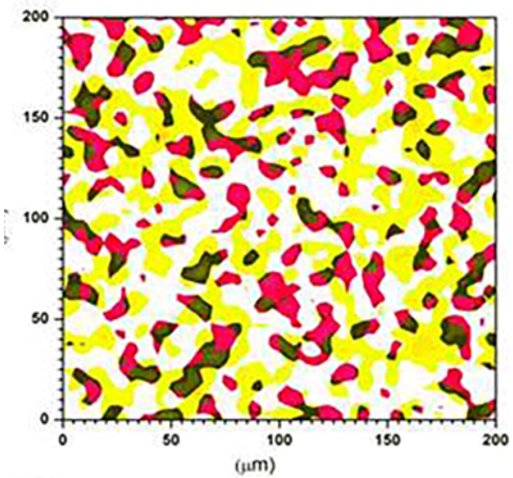
- **In 4M solutions, *Li coordination shell is mixed* (solvent and salt, & PS species in Li/S batteries). Very complex networks formed**
- **Near the electrode surface, work for desolvation (during plating) changes because the salt components are much easily decomposed than the solvents, → $Li^+$ environment changes: it may be strongly bonded to *salt decomposition products***
- **The *simultaneous* SEI formation and Li plating modify the structure of the precursors to dendrite formation**

**Milestone Q2/Y3:** Development of stable electrolytes ✓

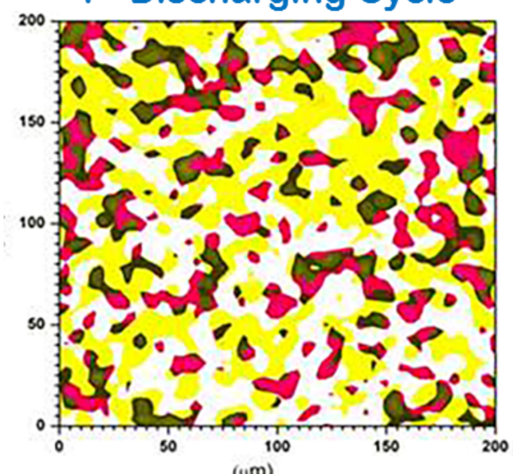
# Technical Accomplishments: XPS and AIMD elucidate SEI structure & composition on Li surface

## XPS chemical imaging

### 1st Charging Cycle

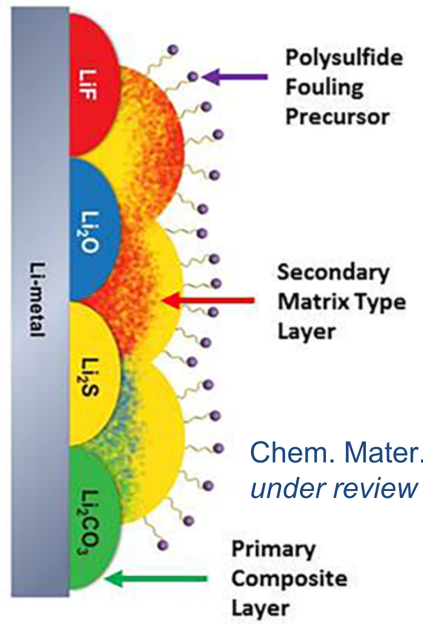



### 1st Discharging Cycle



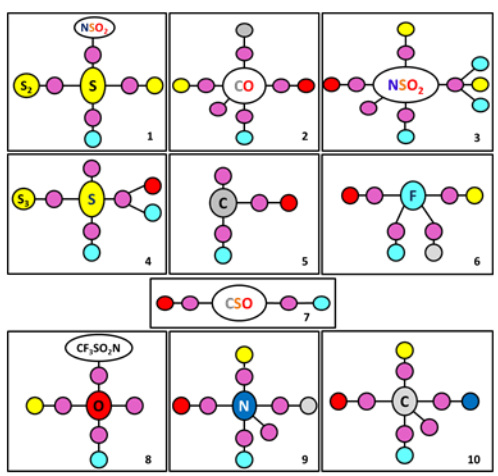

Li-F
PS ($S^0$ species)
Overlap

## SEI Layer Growth



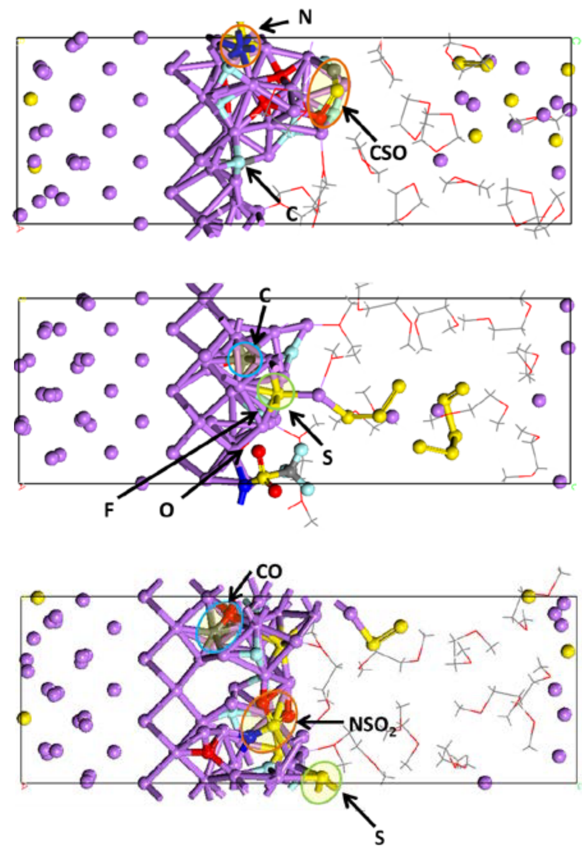

Chem. Mater. **2017**, *under review*

## Fluorine based Li-F from AIMD




Collaboration with Vijayakumar, PNNL

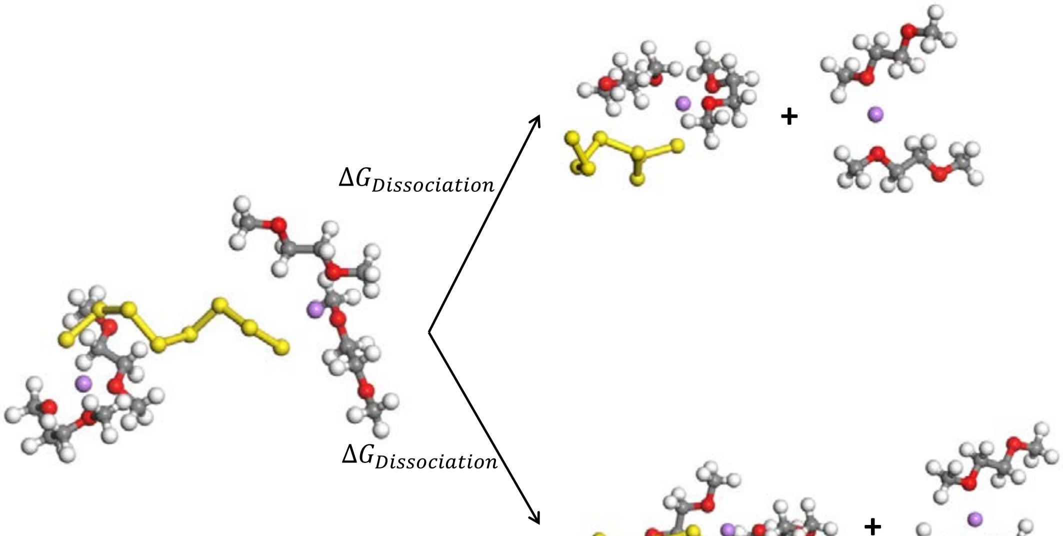
## Predicted SEI Structures from AIMD



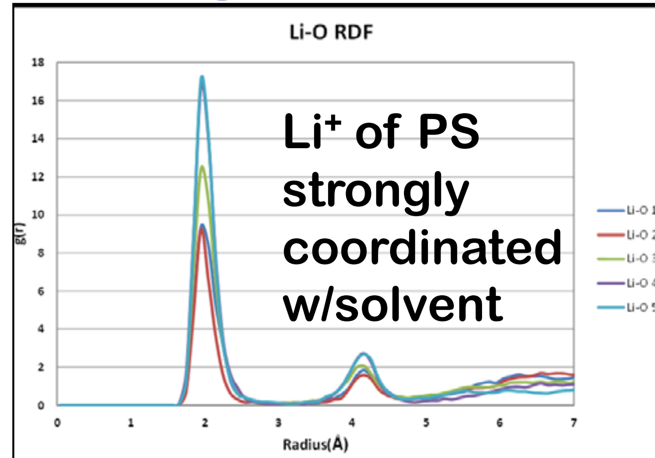

Camacho-Forero *et. al. J. Phys. Chem. C*, **2015**, *119* (48), pp 26828–26839

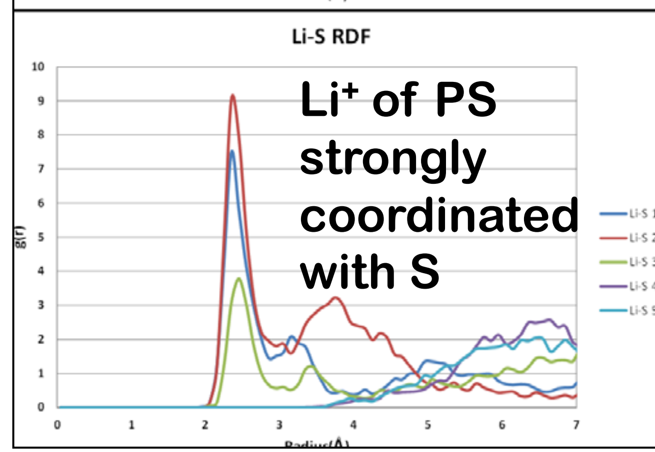
**Milestone Q2/Y3**: Development of stable electrolytes

# Technical Accomplishments:
# Mechanism of polysulfide migration



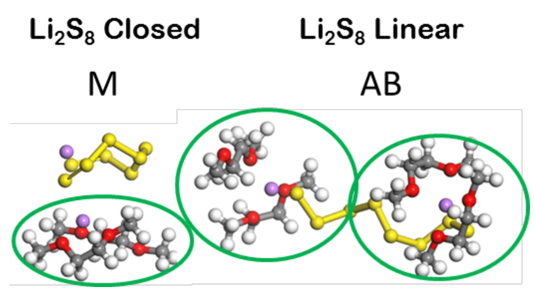

$\Delta G_{Dissociation} = G_{Li-Solvent} + G_{Li-PS} - G_{Li_2PS-Solvent}$




- PS anion formation **is not** favored in many situations
- PS **most likely exists as neutral** species paired with $Li^+$ ions

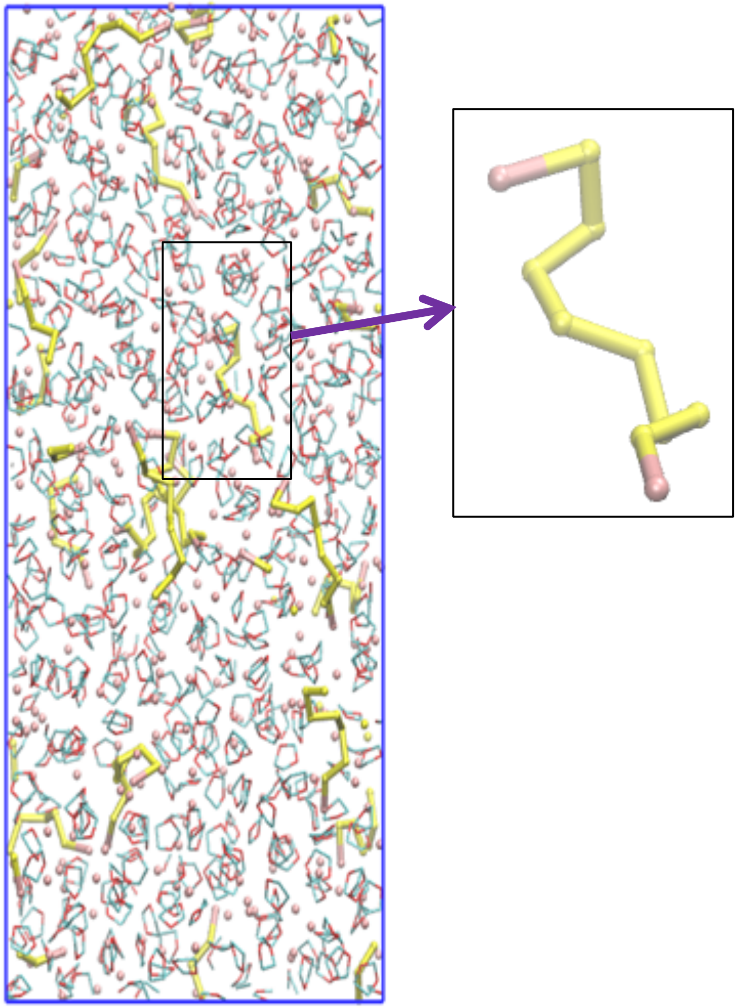
| Structures that favor Ionic Dissociation | | |
|---|---|---|
| DME | 1st Li+ ion | 2nd Li+ ion |
| $Li_2S_6$ | N/A | N/A |
| $Li_2S_8$ Closed | M, J | N/A |
| $Li_2S_8$ Linear | S,J,Z,T,M,U,AB | N/A |
| DOL | | |
| $Li_2S_6$ | N/A | N/A |
| $Li_2S_8$ Closed | N/A | N/A |
| $Li_2S_8$ Linear | N/A | N/A |

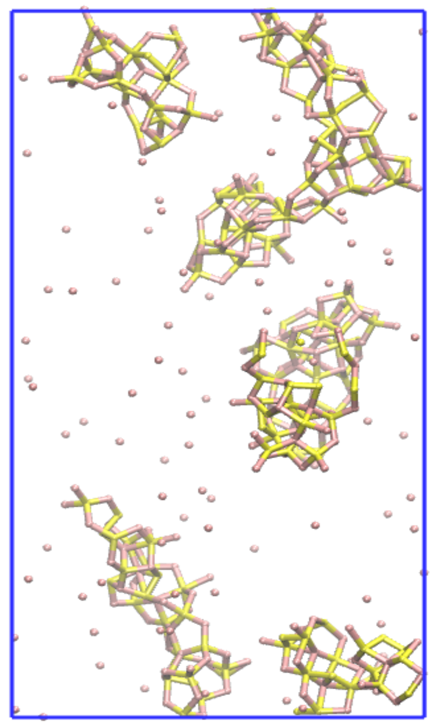



**Milestone Q2/Y3: Development of stable electrolytes** ✓

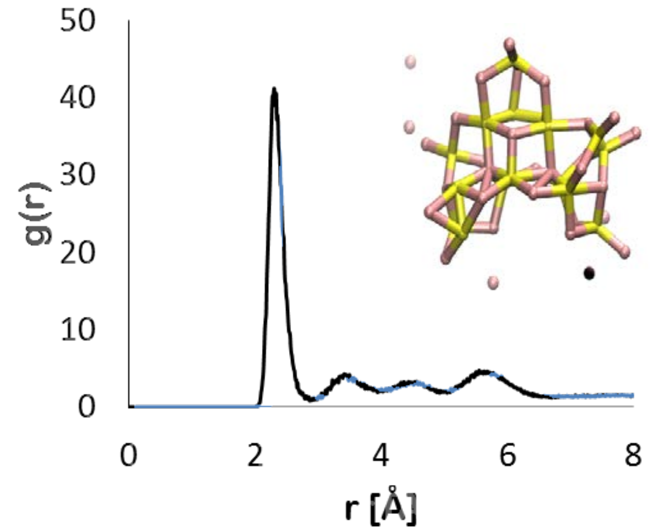
# Technical Accomplishments:
# Mechanism of $Li_2S$ precipitation

**$Li_2S_8$ molecules in DOL liquid phase**





**RDF Li-S @ 2 ns**
**Li/S molar ratio = 1.45**

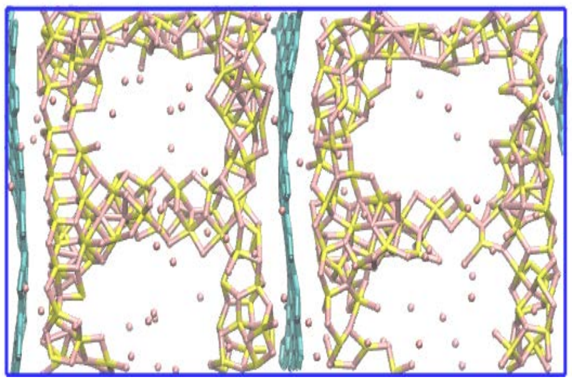



- **Sulfur reduction observed**
- **Li/S structures formed**
- **Li/S structures randomly distributed in liquid phase**

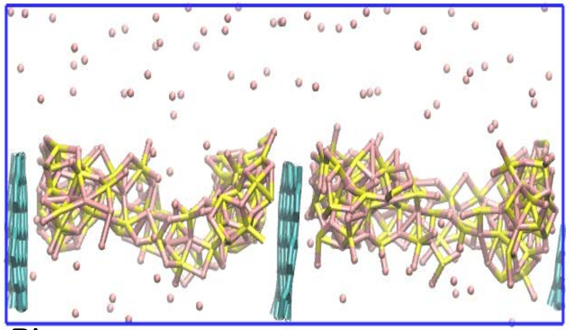
**Milestone Q2/Y3:** Development of stable electrolytes ✓

# Technical Accomplishments:
# Mechanism of $Li_2S$ precipitation

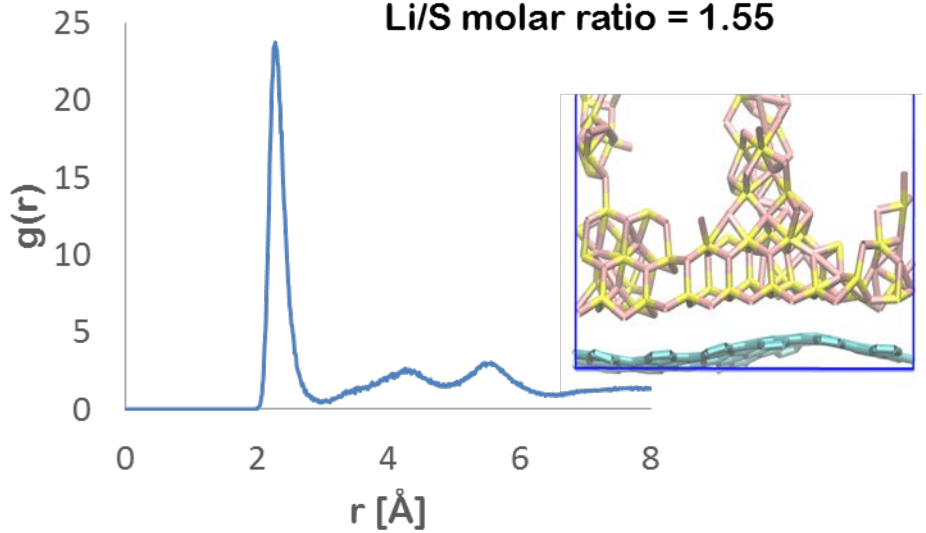
**Reduction of S in 3nm carbon pores**



Plane x-y



Plane x-z

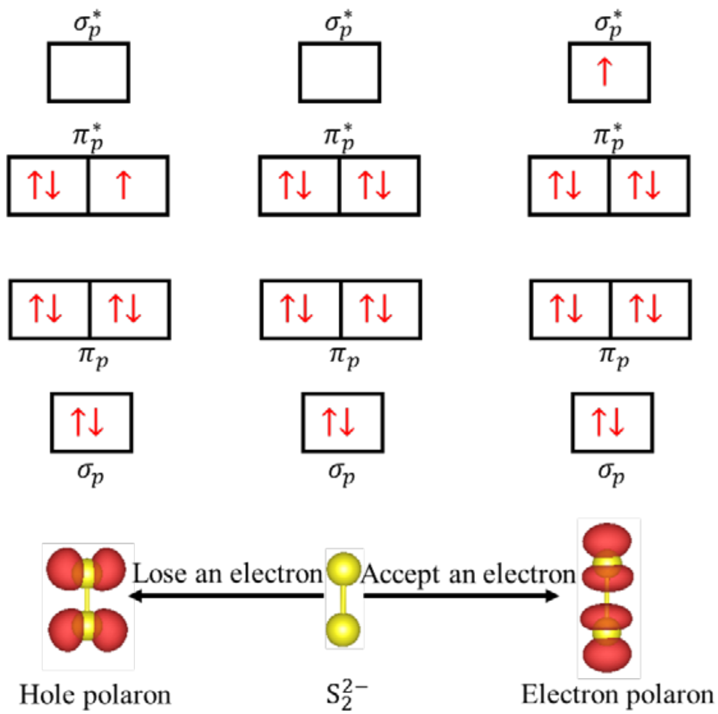



- Li/S structures weakly adhere to carbon layers
- Continuous Li/S structures bridging Graphene layers

**Milestone Q2/Y3:** Development of stable electrolytes ✓

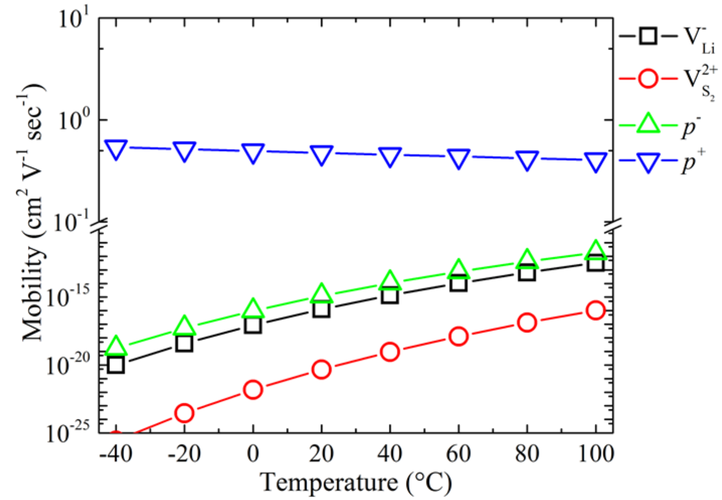
# Technical Accomplishments: Mechanism of Polaron Formation and Diffusion in $Li_2S_2$

identification of charge carriers in insoluble products

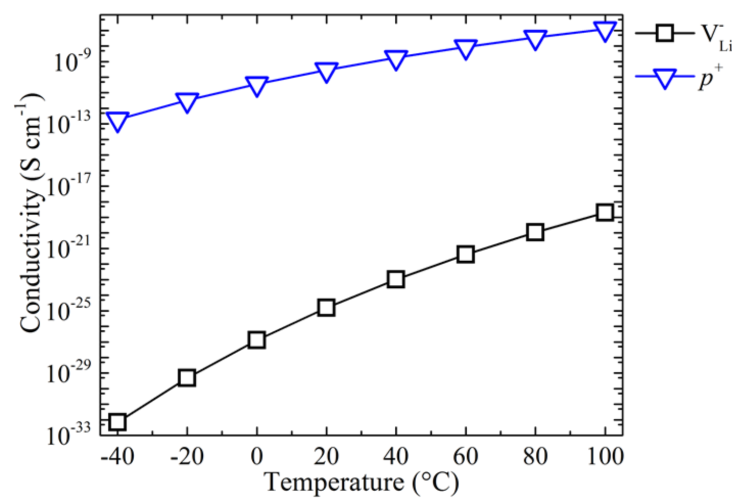



*Schematic diagram of $S_2^{2-}$ polarization mechanism*

*Z. Liu, P. B. Balbuena, and P. P. Mukherjee, "Revealing Charge Transport Mechanisms in $Li_2S_2$ for Li-Sulfur Batteries", *Journal of Physical Chemistry Letters*, **8**, 1324 (2017).



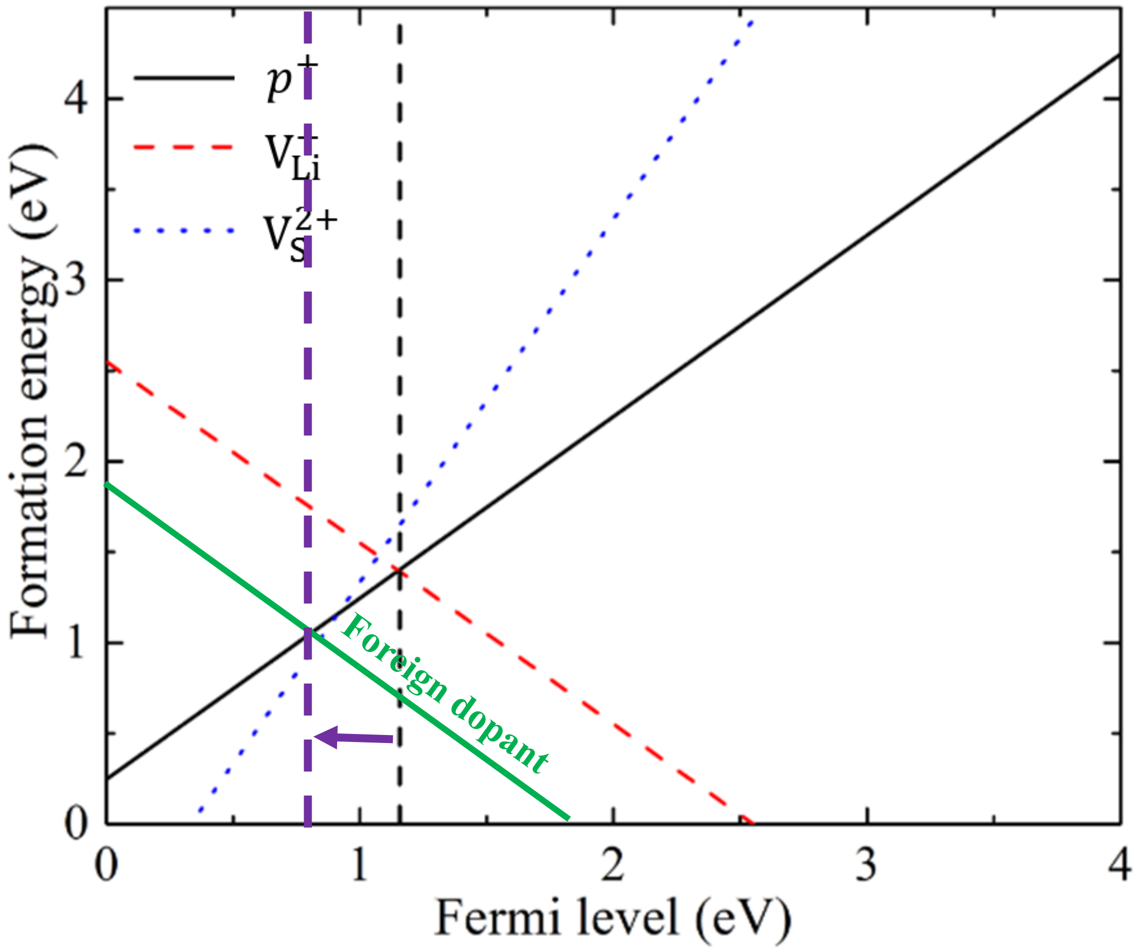

*Effects of temperature on defect mobility*




*Effects of temperature on ionic conductivity and electronic conductivity*

**Milestone Q1/Y2: Development of stable electrolytes**

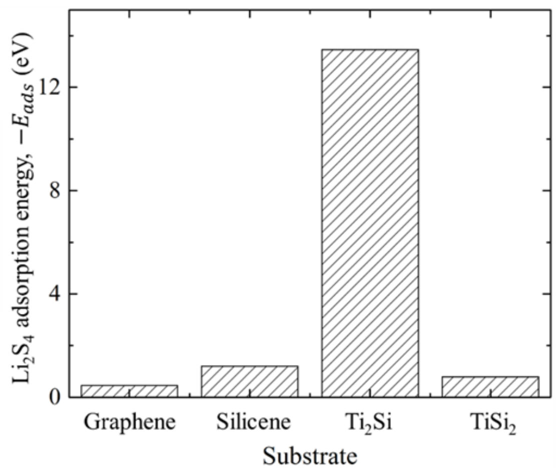
# Technical Accomplishments: How to increase the electronic conductivity of $Li_2S$



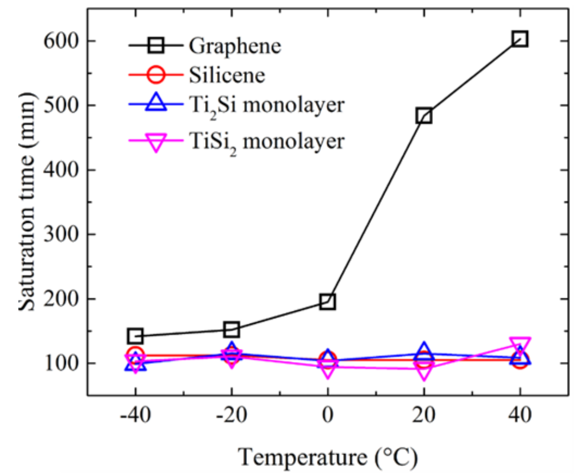

A dopant may help reducing the formation energy of the main carrier of electronic charge

**Milestone Q2/Y3:** Development of stable electrolytes

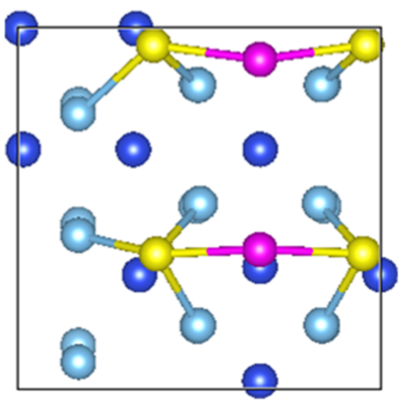
# Technical Accomplishments:
# Cathode material beyond carbon?




$Li_2S_4$ retention on different cathode surface

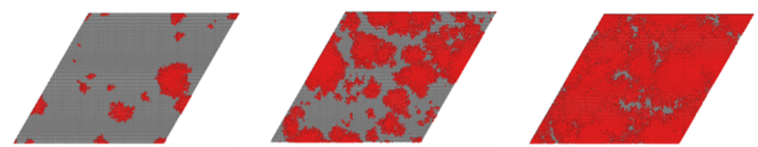



Surface passivation caused by $Li_2S$ precipitation

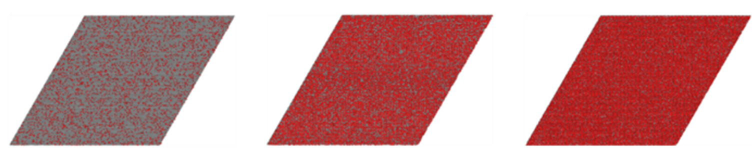


$Li_2S_4$ dissociate to $LiS_2$ on $Ti_2Si$ monolayer

$Li_2S$ formation on graphene: heterogeneous growth



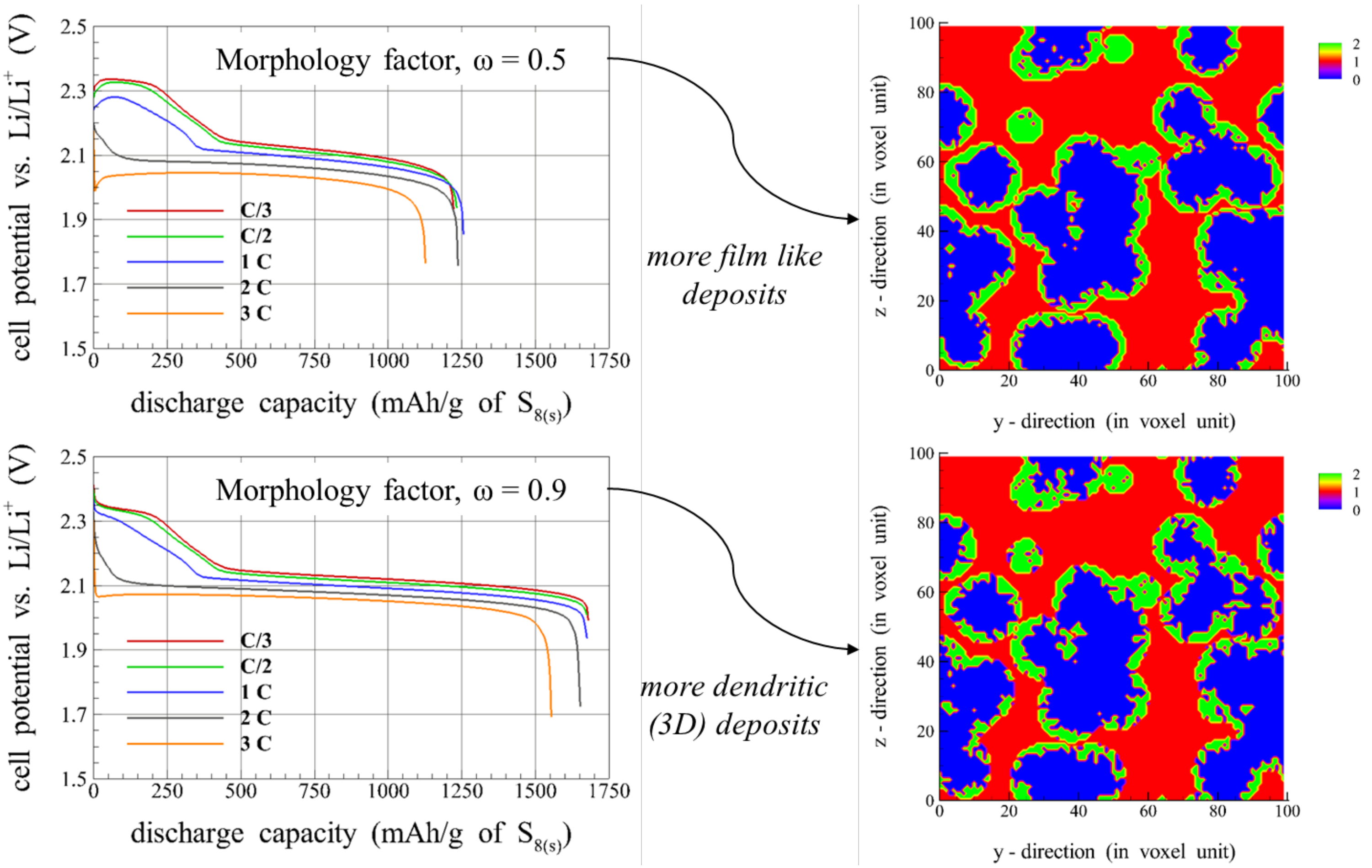
$Li_2S$ formation on silicone or $Ti_2Si$: homogeneous growth



*Liu, Balbuena and Mukherjee, *J. Coordination Chemistry*, **69**, 2090 (2016)
*Liu, Balbuena and Mukherjee, *JOM*, **under review**

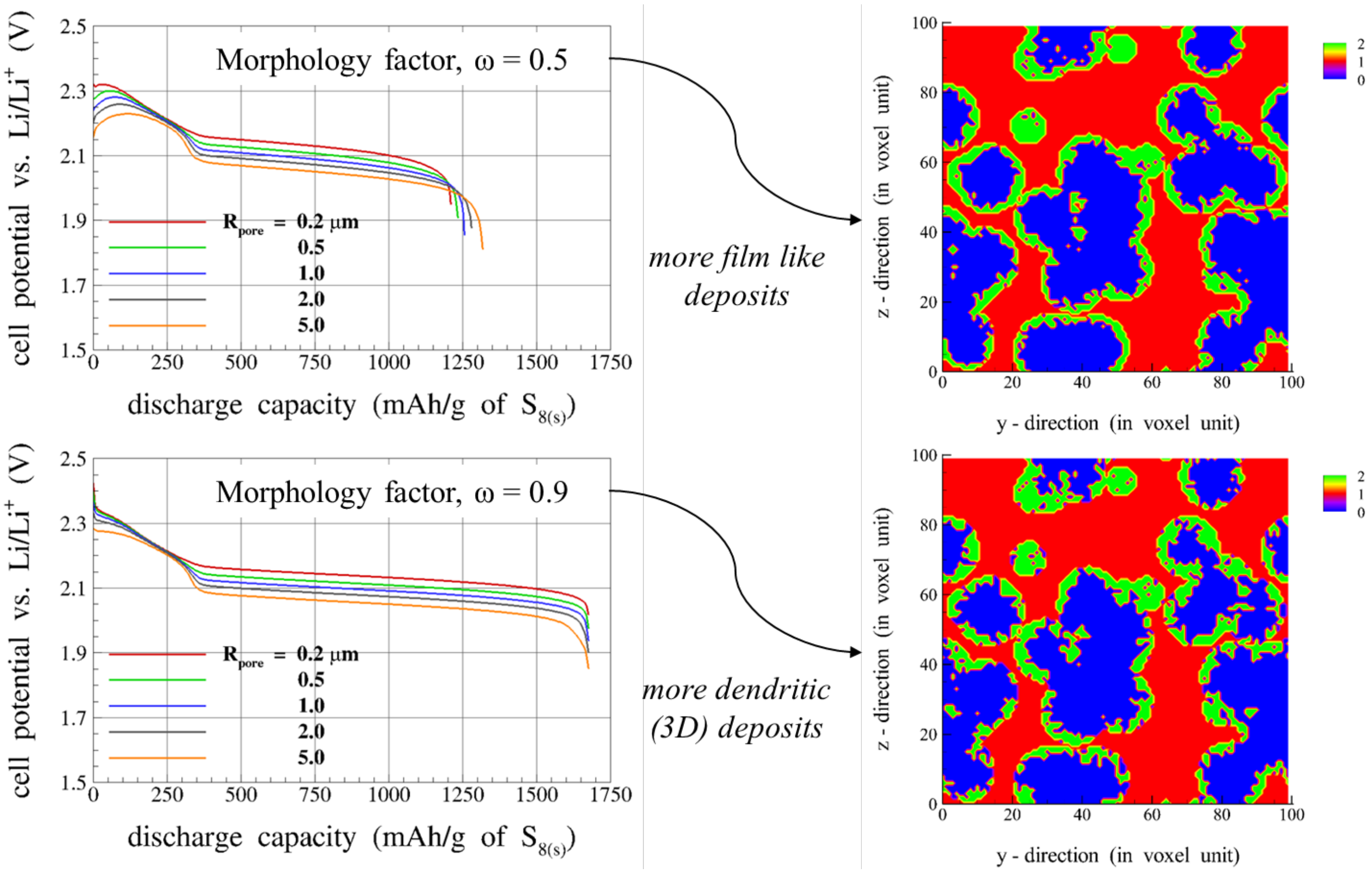
**Milestone Q2/Y1**: Characterization of thermodynamics of nucleation and growth of PS deposits on the Li surface

# Technical Accomplishments: Effect of deposits morphology & C-rate on cell performance



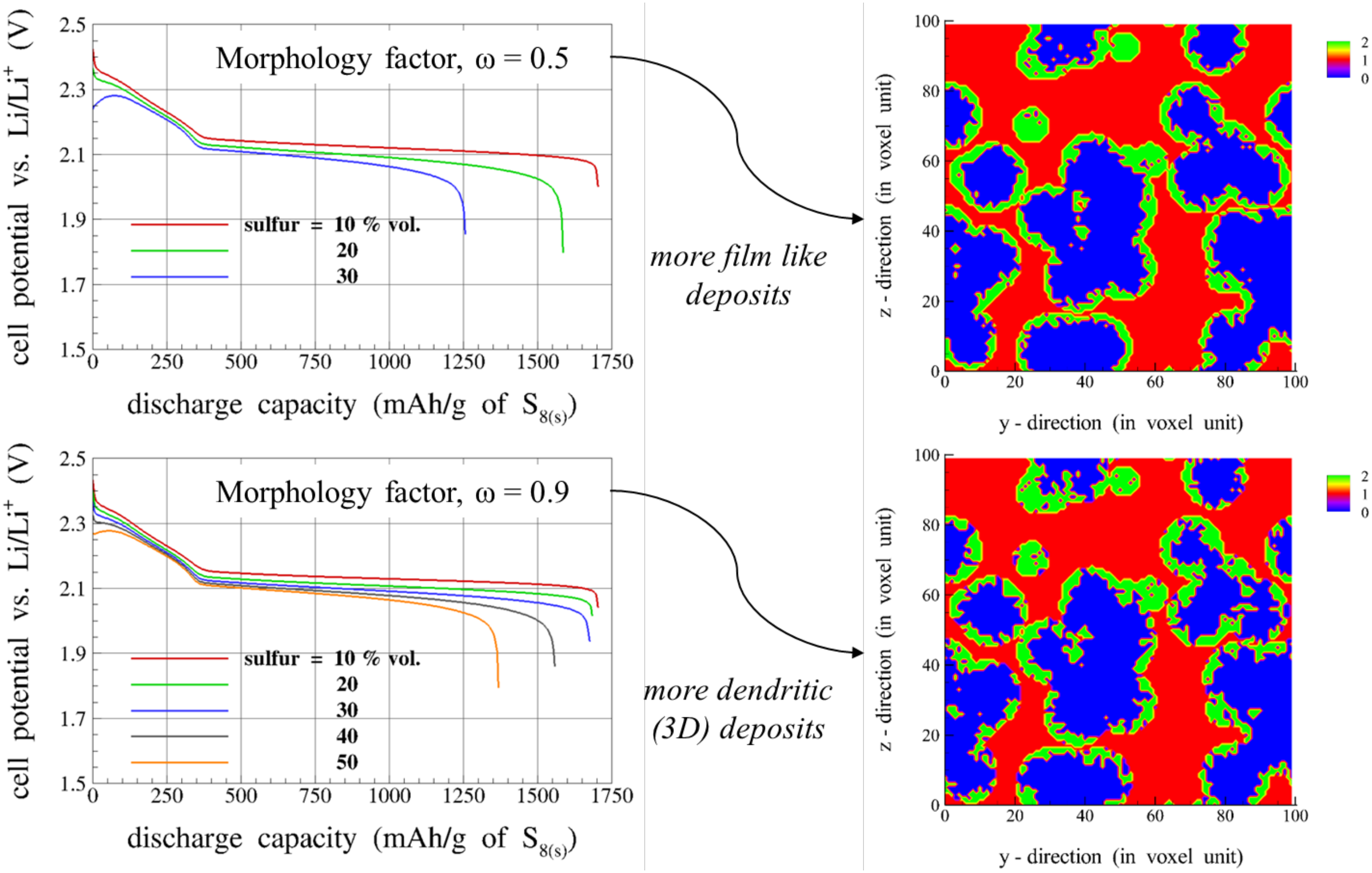

**Milestone Q2/Y1:** Electrochemical modeling of cell performance with electrolyte and cathode parametric properties

# Technical Accomplishments: Interplay of pore size and deposits morphology




**Milestone Q2/Y1:** Electrochemical modeling of cell performance with electrolyte and cathode parametric properties

# Technical Accomplishments: Interplay of sulfur loading and deposits morphology



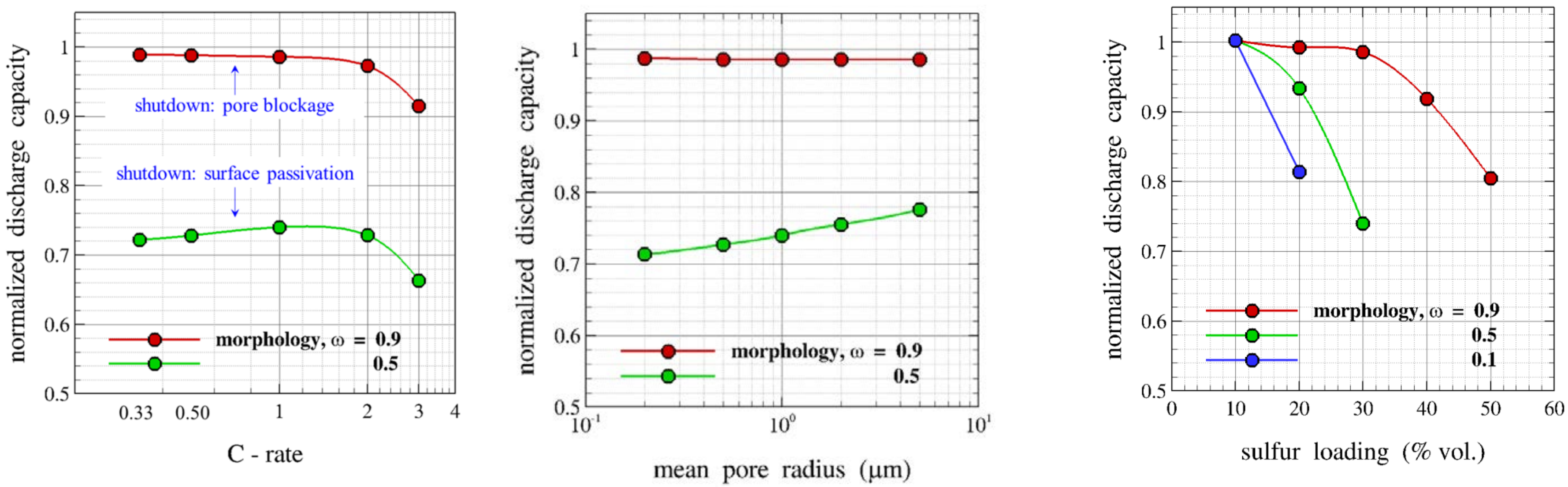

**Milestone Q2/Y1:** Electrochemical modeling of cell performance with electrolyte and cathode parametric properties ✓

# Technical Accomplishments

## Summary of Shutdown Mechanisms

$\omega = 0 \rightarrow$ 2D film

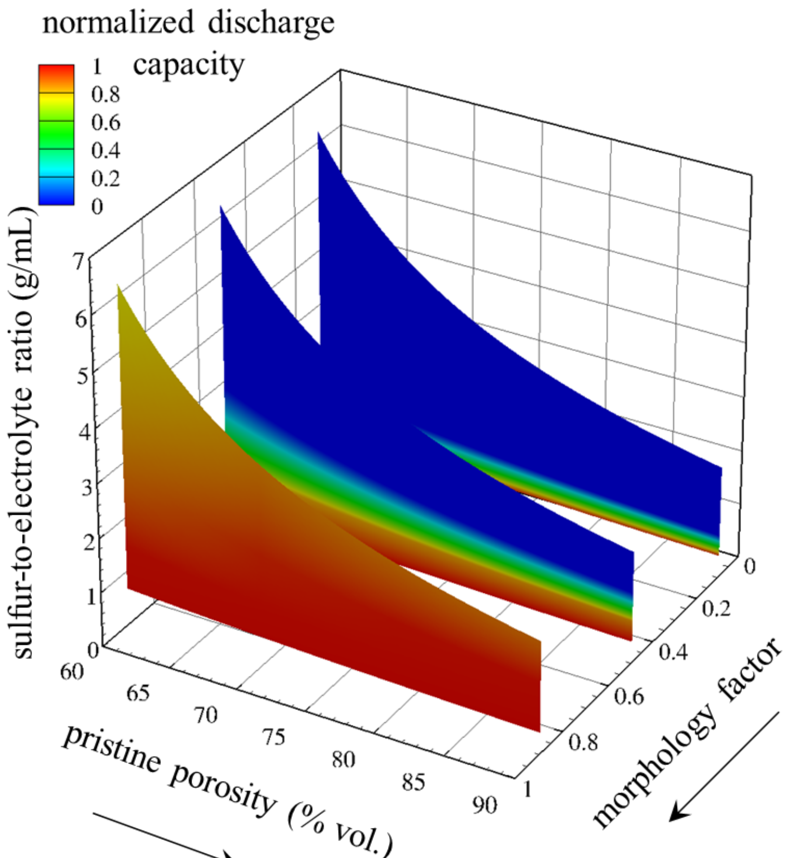
$\omega = 1 \rightarrow$ 3D precipitate (dendrite type)

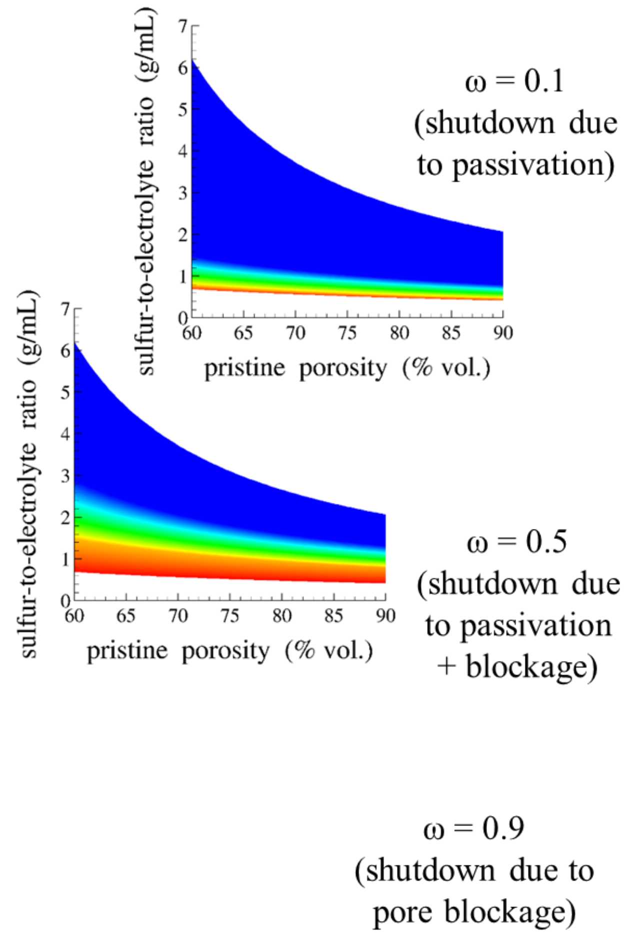



Precipitates morphology leads into different shutdown mechanisms

**Milestone Q2/Y1:** Electrochemical modeling of cell performance with electrolyte and cathode parametric properties

# Technical Accomplishments
## Regimes of Li/S operation



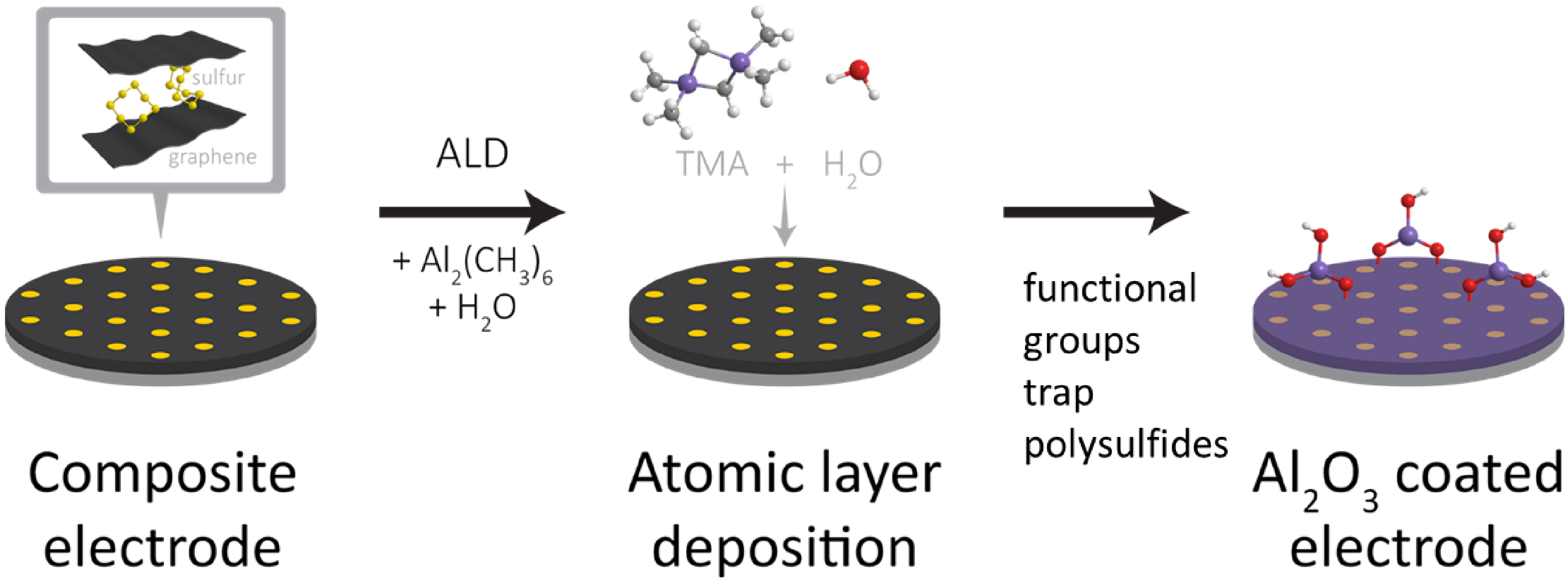




*Mistry and Mukherjee, *Identifying feasible sulfur-to-electrolyte ratio for lithium-sulfur cells: microstructural limitations*, (in preparation)

**Milestone Q2/Y1:** Electrochemical modeling of cell performance with electrolyte and cathode parametric properties

# Technical Accomplishments
## PS retention: Experiments

### $Al_2O_3$ coated graphene with nanosulfur: preparation



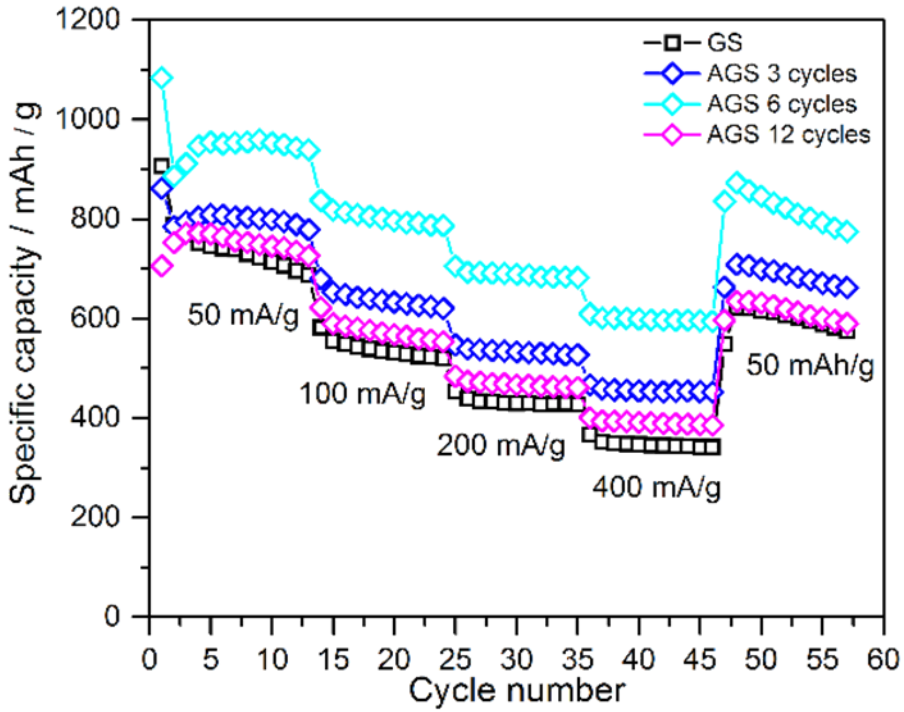

Laminates prepared with the graphene-sulfur composite, super P, and PVDF binder

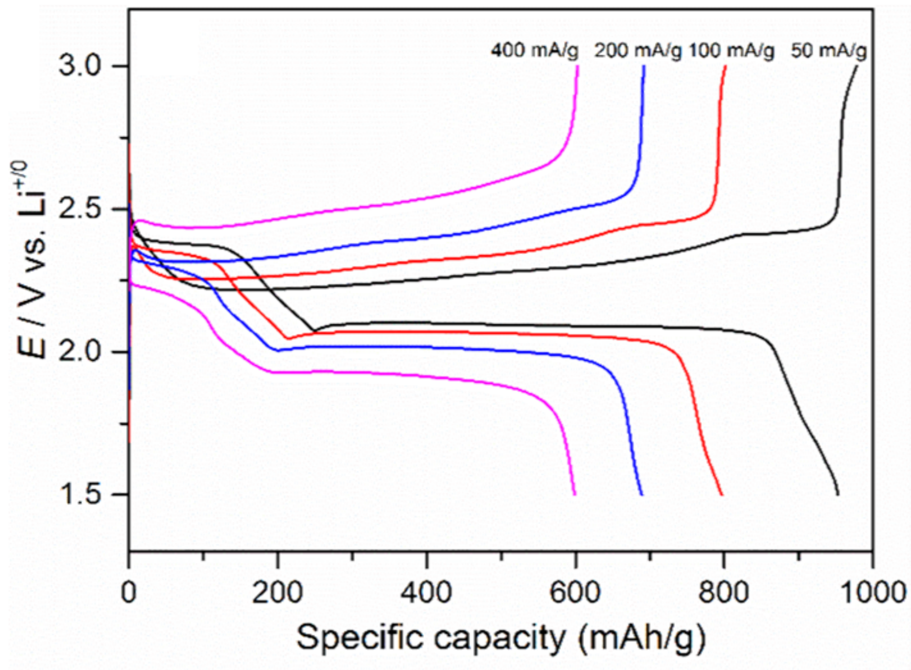
Laminates were coated with $Al_2O_3$ via atomic layer deposition (ALD) by trimethyl Al decomposition with water

Various ALD cycle times control the effective $Al_2O_3$ coating thickness

# Technical Accomplishments
## PS retention: Experiments

### $Al_2O_3$ coated graphene with nanosulfur: Electrochemical performance

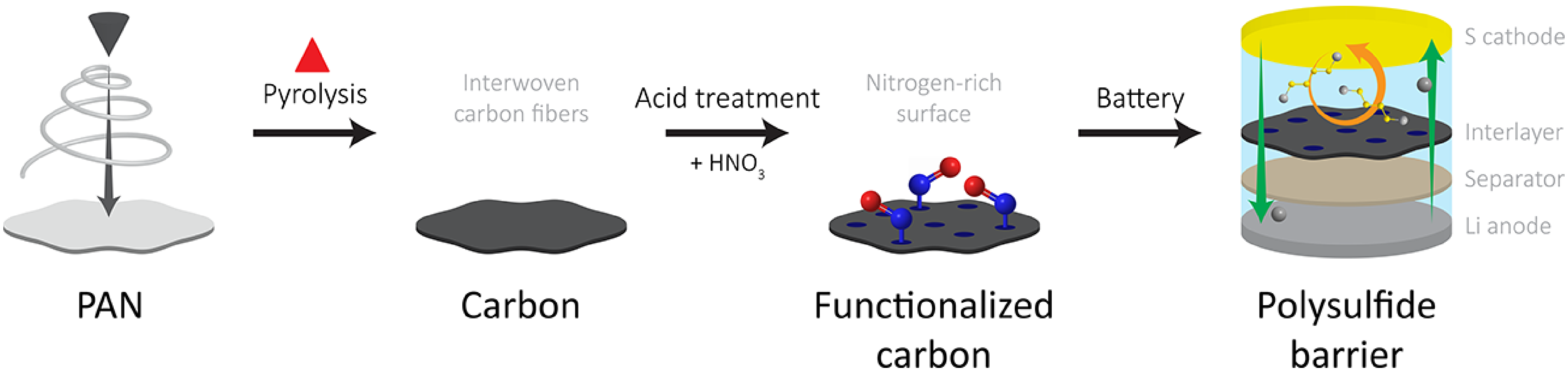



$Al_2O_3$ coating increases capacity at all rates
A 6-cycle ALD coating (light blue) produces the highest specific capacity
As applied specific current increases, voltage hysteresis increases for 6-cycle ALD coating

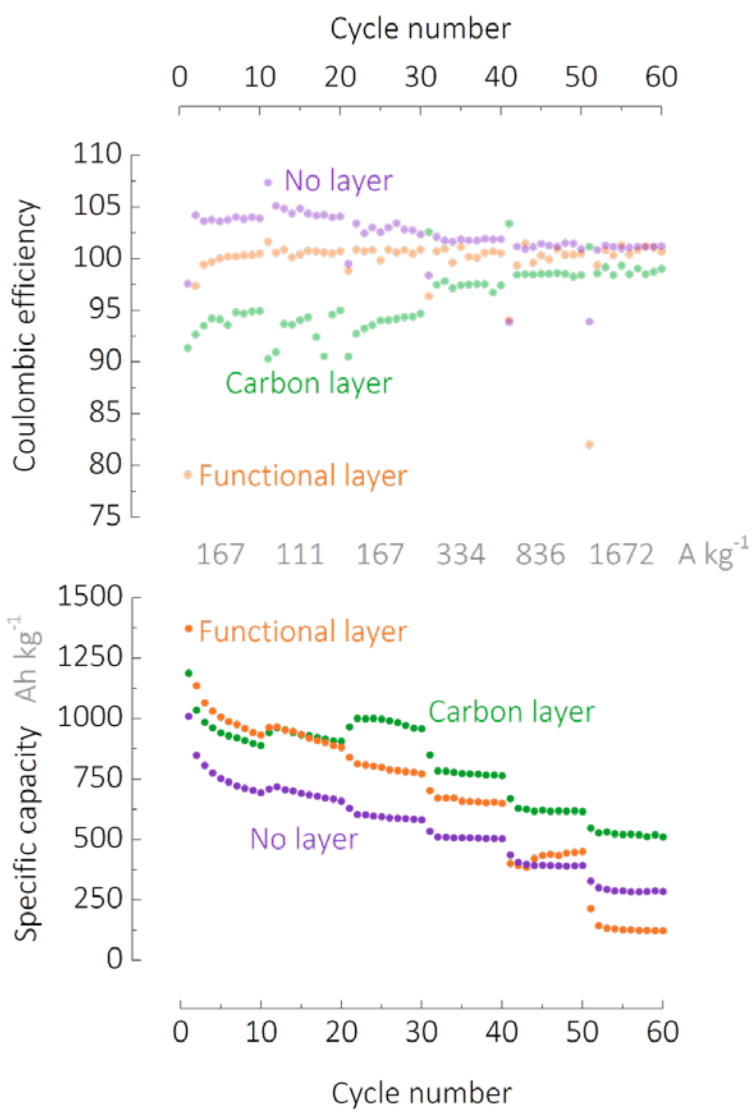
# Technical Accomplishments
## PS retention: Experiments

### Functionalized Carbon Interlayers: Preparation




Polyacrylonitrile fibers are formed and woven into a cloth-like membrane via *electrospinning*
Treatment with nitric/sulfuric acid functionalizes the surface of the cloth
The functionalized cloth exhibits improved performance for Li/S batteries

# Technical Accomplishments
## PS retention: Experiments
### Functionalized Carbon Interlayers: Electrochemical Performance




The functionalized interlayer shows the most stable Coulombic efficiency across all studied rates

The functionalized interlayer has highest initial capacity, but the carbon interlayer shows better rate capability

The functionalized interlayer improves rate capability relative to no interlayer at currents >334 A kg-1 (~ C/5 rate)

# Responses to Previous Years Reviewers' Comments

Comment 1: "As with all molecular level models, the concern will be whether it represents to real-world problems in a meaningful way."

Answer: By carefully going through the current presentation, the Reviewer can verify that the molecular models are realistic, As an example, we show that our simulations are able to predict the SEI composition on a Li metal anode in presence of polysulfides, and contribute to elucidate XPS spectra (see slide 11)

Comment 2: "no much synergy between the simulations and synthesis/testing so far"

Answer: The simulations have pointed out and explained most of the issues found by the electrochemical performance experiments (for example surface passivation, pore blockage, materials used for PS retention inducing $Li_2S$ deposition).

# Responses to Previous Years Reviewers' Comments

Comment 3: "the project team has limited collaborations."
Comment 4: "recommended that the project team adopt the advanced characterization methods available in national laboratories to link the simulations with materials structure and morphology.

Answer: Besides the collaborative work with ANL and PNNL mentioned in the previous report, new collaborations are in place with PNNL (Dr. Vijayakumar, XPS experiments), as suggested in Comment 4.

Comment 5: "need of more specific plans regarding future work, such as how to identify the reasons for failures and successes of specific electrolyte compositions."

Answer: This report contains extensive details regarding the specific question of the reviewer. We have elucidated the reasons for success of concentrated salt solutions.

# Collaboration and Coordination with Other Institutions

- Purdue University: This project is a collaboration between Texas A&M University (Balbuena, Mukherjee) and Purdue University (Pol). The groups communicate via teleconference and site visits.
- Pacific Northwest National Laboratory (PNNL): The TAMU team interacts with the group of  Dr. Jason Zhang regarding analysis of strategies to mitigate extreme Li metal reactivity. We have investigated the reasons for the apparent mitigation effects caused by high salt concentrations as a function of the nature of the salt.
- Argonne National Laboratory (ANL): Dr. Vilas Pol (Purdue) collaborates with the group of Dr. Jeffrey Elam and Dr. Anil Mane at ANL in the applications of ALD coatings for polysulfide capture at the cathode.
- Pacific Northwest National Laboratory (PNNL): The TAMU team interacts with the group of  Dr. M. Vijayakumar regarding SEI characterization on LI
- metal surfaces in presence of polysulfides via XPS and AIMD simulations.

# Remaining Challenges and Barriers

- Evaluate hypothesis developed in this work on effects of high salt concentrations on **dendrite formation at the Li metal anode**.
- Evaluate effects of dopants suggested in this work on **$Li_2S$ conductivity**.
- Optimize cathode morphology to overcome **shutdown effects** identified in this work.
- **Scale up** of cathode composites.

# Proposed Future Work

- **Rest of FY17**:
  - continue the development of stable electrolytes and efficient cathode morphologies
  - produce 3-5gr of C/S composite and achieve capacity > 800 mAh/g during at least 400 cycles

Any proposed future work is subject to change based on funding levels

# Summary Slide

- **Relevance:** Overcome Li-metal anode deterioration issues via protective passivation layers and minimizing polysulfide shuttle with advanced cathode structure design.
- **Approach:** Synthesis, characterization, and testing of a C/S composite cathode guided by multiscale modeling (atomistic and mesoscopic) focusing on electrolyte composition and cathode morphology effects on cell performance.
- **Technical Accomplishments:** Identification of effects of high concentrated solutions on SEI formed at lithium anode surfaces and potential effects on Li dendrite morphologies; theoretical and experimental characterization of SEI formed on Li metal in presence of PS species; identification of effects of Li2S deposition modes on shutdown mechanisms. Synthesis and tests of PS retention materials.
- **Collaborations:** Purdue University (Co-PI); evaluation of additives, salts, and SEI (with PNNL); cathode coatings (with ANL).
- **Future Work:** Development of stable electrolytes; scale up cells and achieve target capacity; model effects of cathode microstructure on cell performance.